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**IPST Technical Paper Series Number 914**

On-Line Monitoring of Sulfide, Alkali, and Carbonate by an ATR-UV Sensor  
During Borate Autocauticizing Mill Trials

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July 2001

Submitted to  
Process Control and Quality

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# **On-Line Monitoring of Sulfide, Alkali, and Carbonate by an ATR-UV Sensor During Borate Autocausticizing Mill Trials**

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## **ABSTRACT**

The recent advances in understanding the borate autocausticizing process indicate that partial substitution of calcium oxide with borate could be a very attractive and economical way to reduce the energy cost in lime kilns in kraft mill operations. Accurate and timely analysis of sulfide, hydroxide, and carbonate concentrations in recausticizing process liquors is essential to the successful mill trials of borate autocausticizing. Unfortunately, the traditional ABC titration method fails in analyzing the hydroxide, sulfide, and carbonate concentration due to the presence of borate. This paper demonstrates an ATR-UV spectroscopic sensor for rapid and simultaneous determination of sulfide, hydroxide, and carbonate in kraft liquors that contain borate. The results of on-site mill trials showed good agreements between the ATR-UV method and the ABC titration method combined with the atomic absorption method. The ATR-UV technique is rapid, simple, and can be used for on-line process control.

**Keywords:** Sulfide, Effective alkali, Carbonate, Attenuated total reflection (ATR), UV, White liquor, Green liquor, Borate, Autocausticizing.

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## INTRODUCTION

Kraft pulping employs an aqueous solution, often called white liquor, of sodium hydroxide (NaOH) and sodium sulfide ( $\text{Na}_2\text{S}$ ) to remove lignin from wood. Wood chips are subjected to digestion in the white liquor at an elevated pressure (about 8 atm) and temperature (about  $170^\circ\text{C}$ ) in a pressure vessel (digester) to release cellulosic fibers. The spent pulping liquor containing dissolved wood lignin, often called black liquor due to its color, is concentrated and then burned in a recovery furnace where sulfur compounds are reduced to sodium sulfide. The smelt of inorganic ash from the combustion processes is dissolved in water to form green liquor, named for its color, containing mostly sodium sulfide, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). The sodium carbonate reacts with calcium hydroxide (calcium oxide in water) in a process known as recausticizing to regenerate sodium hydroxide to remake the white liquor for pulping. The lime mud (mainly calcium carbonate) yielded from the recausticizing reaction is burned in a lime kiln to produce the calcium dioxide. A chemical recovery cycle consists of all the processes from the concentration of the pulping spent liquor to the regeneration of sodium hydroxide.

The quality of the white liquor, or more precisely the concentrations of the active cooking chemicals, i.e., effective alkali ( $\text{EA} = \text{NaOH} + 1/2 \text{Na}_2\text{S}$ ) and sulfide (refer to  $\text{Na}_2\text{S}$ ), and the dead-load species in the liquor, such as carbonate (refer to  $\text{Na}_2\text{CO}_3$ ), have significant impact on the pulping operation in terms of pulping delignification rate and pulp quality. The quality of white liquor strongly depends on how well the recausticizing operations are monitored and controlled. In current mill practice, the concentrations of EA, sulfide, and carbonate in each unit stage of the recausticizing operation are determined using an off-line titrimetry called the ABC titration method [1]. The method uses the standard hydrochloride acid to titrate the sample. There are three titration end points, i.e., A, B, and C, on the pH coordinate that are related to masses of EA, sulfide, and carbonate in the sample, respectively. The ABC method has been used as a reference method in the developing of novel instruments for the analysis of alkali, sulfide, and carbonate in kraft liquors [2-7].

Using borate to achieve autocausticization for pulping chemical recovery has attracted some attention from the pulp and paper industry in the past. Borate in kraft black

liquor reacts with sodium carbonate to form sodium borate in the recovery furnace. The sodium borate hydrolyzes in water and produces sodium hydroxide and borate [8-10]. High borate load has the potential of eliminating the lime kiln process, but could negatively affect the pulping and black liquor evaporation operation. A recent study by Tran et al. [11], however, suggests that the amount of borate charge could be reduced by 50% while releasing the same amount of hydroxide. Therefore, at relatively low-level charge, <25% of the stoichiometry requirement, it can reduce the fuel consumption in the lime kiln without influencing other operations. This discovery led to renewed interest in the borate autocausticizing process. Mill trial runs have been initiated in a couple of North America mills.

Borate is a weak base salt that affects the titrametric curve during ABC titration, causing the inflection points corresponding to hydroxide and sulfide to become indistinct and to shift. Using the fixed pH value to indicate the end point of titration was found to overestimate the concentrations of these components due to the presence of borate in the process kraft liquors. Therefore, the conventional ABC titration method fails to analyze the concentrations of EA, sulfide, and carbonate. Presently, no single method can determine these three key components in the liquors containing borate. To resolve this analytical problem, US Borax Corp. (Valencia, CA, USA) developed a modified ABC procedure using several analytical methods to measure the three components in borate-containing liquors. The liquor was first analyzed by the ABC titration method. The effect of borate on the titration results was then accounted for by either using atomic absorption spectroscopy to determine boron, or silver nitrate titration to measure sulfide concentration. Some procedure is fairly complicated and time-consuming to use for routine analysis. Therefore, the boron concentration in the process liquor was often measured only once a day. Process control is not possible with the off-line ABC titration method.

Attenuated total reflection (ATR) or internal reflection spectroscopy was developed in the 60s [12, 13]. Because the absorption path length of the evanescent wave is greatly reduced to the order of micron meters, ATR is particularly useful for the analysis of concentrated liquid samples without dilution. Chai et al. [14, 15] demonstrated the

feasibility of analyzing NaOH and Na<sub>2</sub>S concentrations simultaneously in a synthetic white liquor with ATR-UV and also successfully performed in-line determination of both sulfide and polysulfide in a lab-scale unit of electrochemical production of polysulfide from a synthetic white liquor. More recently, we successfully developed an ATR-UV sensor to simultaneously determine alkali, sulfide, and carbonate in conventional kraft white and green liquors (i.e., without borate) [6, 7]. During an on-site mill trial, good agreements of measured EA, sulfide, and carbonate in the conventional kraft white liquors have been achieved between the ATR-UV method that uses a linear calibration procedure and the conventional ABC titration method [7].

In this work, we investigated the feasibility of using ATR-UV technology to analyze the EA, sulfide, and carbonate concentrations in the borate-containing kraft white liquor at a kraft mill site.

## METHODOLOGY

We have derived the ATR absorption spectral intensity,  $A_\lambda$ , at the given wavelength in a previous study [14] based on the basic ATR principles in the literature [12, 13]. For an ATR system with  $z$  reflections, we found

$$A_\lambda = k \cdot z \left[ (\varepsilon_1 C_1 + \varepsilon_2 C_2 + \dots + \varepsilon_n C_n) \cdot b_{eff}(C_1, C_2, \dots, C_n, \lambda) \right] \quad (1)$$

where  $k$  is the instrument response function of the ATR system, which includes the responses of the detectors and optical components and the slit transfer function of the spectrometrometer.  $b_{eff}$  is the effective optical path length of the ATR probe.  $\varepsilon_i$  and  $C_i$  are the absorption coefficient and molar concentration, respectively, of species  $i$  in the liquor.  $\lambda$  is wavelength of interest. If the variation of the effective optical path length is not significant and can be neglected, then, Eq. (1) can be simplified as,

$$A_\lambda = f_1^\lambda \cdot C_1 + f_2^\lambda \cdot C_2 + \dots + f_n^\lambda \cdot C_n \quad (2)$$

where  $f_i^\lambda = z b_{eff} \cdot k_i \varepsilon_i$  are wavelength-dependent calibration constants.

## **EXPERIMENTAL APPARATUS AND PROCEDURE**

All measurements were conducted in a laboratory ATR-UV system that is described elsewhere [6,7]. The system as shown in Fig. 1 consists of an ATR-UV flow cell with one path (reflection) (Axion, Model TNL-120H23-3, CA, USA) for on-line analysis, a peristaltic pump (RP-1, Rainin, Emeryville, CA, USA), a 25-mL beaker, tubing and connectors, and a UV/Vis spectrophotometer (UV-8452, Hewlett-Packard, now Agilent Technologies, CA, USA). The ATR cell consists of an ATR probe made of a quartz rod and a housing unit.

The hot liquor sample was taken from the mill recausticizing unit. After being cooled to room temperature in running tap water, the sample was circulated into the ATR flow cell without dilution for direct UV absorption measurements. The absorption spectrum in a wavelength range of 190–270 nm was recorded. The concentrations of the alkali, sulfide, and carbonate in a conventional (without borate) kraft liquor were first determined by the ABC titration method. The results were then used to calibrate the ATR-UV method for simultaneous determination of alkali, sulfide, and carbonate in borate-containing white liquors from the UV absorption spectral data. The results obtained by the ATR-UV method were compared with those measured by the atomic absorption together with the ABC titration method developed by US Borax.

## **RESULTS AND DISCUSSION**

### **Effect of Borate on ATR-UV Absorption Spectrum**

Borate acts as a weak base in titration; it fails the ABC titration method for sulfide, alkali, and carbonate determinations in kraft liquors. Fortunately, the examination of the borate solution indicates that borate does not absorb UV light even at a relatively high borate charge (define), e.g., about 25 %. However, due to the nature of ATR spectroscopy, the refractive index of a solution also contributes to the ATR absorption spectrum by altering the effective optical absorption path length [14]. At very high concentrations, borate can change the refraction index of kraft liquor and therefore affect the ATR-UV absorption spectrum. Figure 2 shows the typical ATR-UV spectra of kraft white liquor with different borate charges. The results indicate that there are no significant spectral variations

up to a borate charge of 11%. It becomes evident that the spectral intensity increases across the entire absorption wavelength range when the borate charge is higher than 11%.

To further study the effect of borate on the ATR spectrum of white liquors, we plotted the absorption at three specific wavelengths, i.e., 197, 200, and 230 nm, that are selected for quantifying carbonate and/or effective alkali and sulfide, respectively. Figure 3 shows the effect of the borate charge in the liquors on the absorption spectral intensities at these three wavelengths. The absorptions at wavelengths of 230 and 200 nm are from sulfide and hydroxide, respectively. As expected, the borate charge on the spectral intensity is nonlinear and becomes significant only at a borate charge greater than 10%. With a borate charge of 17%, the absorption intensities at these three wavelengths are about 3- 8 %, depending on the wavelength.

### **Calibration**

As we mentioned previously, the refraction index can contribute to the absorption spectrum in ATR spectroscopy by altering the effective optical path length, which makes calibration rather complicated. This is because the refraction index of a solution is often a function of the species concentrations to be determined. However, as we demonstrated in our previous study [7], in normal kraft recausticizing operations, the variation of the concentrations of the three key species (sulfide, alkali, and carbonate) is not great enough to alter the optical path significantly to affect ATR measurements. Therefore, the effect of spectral modification caused by the variation of refractive index can be ignored. Furthermore, we demonstrated that under 10% borate charge the effect of the addition of borate on the ATR absorption spectrum of white liquor is insignificant. The borate charge was 5% during our first mill trial run. Therefore, the linear calibration approach used in conventional absorption spectroscopy can be applied, which significantly simplifies ATR measurements. We used the process liquor without the addition of borate to conduct linear calibration. By using the actual liquor in calibration, we eliminated (or minimized) the effect of refractive index caused by other dead-load chemicals, such as sulfate and thiosulfate, on ATR measurements.



As we found in our previous study [6], hydroxide and carbonate absorb in the range of 190 to 210 nm, while sulfide absorption peaks at 230 nm and below 210 nm as well. We chose the absorptions at 230, 200, and 197 nm to determine the concentrations of sulfide, effective alkali, and carbonate. The ABC titration method was first employed to determine the concentration of these three species in the calibration liquor. Two simple linear equations to calculate sulfide and EA concentration can be obtained based on the absorption intensities at the wavelengths of 230 and 200 nm, respectively:

$$C_{Na_2S} = k_1 A_{230} \quad (1)$$

and

$$C_{EA} = k_2 A_{200} \quad (2)$$

where  $C_i$  is the concentration of a given species  $i$ ,  $k_1 = 284.2$  and  $k_2 = 373.1$  are calibration constants, and  $A_i$  is the absorption value at a given  $i$  wavelength.

To quantify carbonate concentration, an equation is established based on the absorption value at 197 nm and corrected for the contribution of hydroxide ion:

$$C_{Na_2CO_3} = k_3 (A_{197} - k_4 C_{EA}) \quad (3)$$

where  $k_3 = 1775.2$  and  $k_4 = 0.00407$ . The other process parameters, e.g., total titratable alkali (TTA), active alkali (AA), sulfidity, and efficiency of causticization, can be obtained based on the concentrations of these three species that were calculated from Equations (1), (2), and (3).

### Effect of Borate on Measurement Errors

The effect of the addition of borate on ATR measurement error can be accounted for using the spectral data obtained with the addition of a known amount of borate, as shown in Fig. 3. By applying Equations (1) to (3) using the calibration constants obtained, we found that the effect of borate on the measurement errors are within 5% with borate charge less than 15% for sulfide and EA. The effect of borate on measured sulfide concentration is the smallest. The effect of borate on measured carbonate concentration is the greatest. Figure 4 shows the calculated errors in measured carbonate, sulfide, and EA due to borate charge. The data shown in Fig. 4 can be used for correction when the borate charge is known.

## Mill Trial Results

The mill trial of the ATR-UV method to analyze white liquor in a borate autocausticizing operation was conducted during the startup period. The ATR-UV sensor was calibrated by the process liquors before borate was added by the conventional ABC titration method.

During the startup of the borate autocausticizing trial, the concentrations of sulfide, EA, and carbonate in the liquor of the first causticizer were monitored. The level of borate in the liquors was gradually increased to 5% from zero at the end of this three-day period. Figure 5 shows the concentrations of the three components measured using ATR-UV during the three-day period. As a comparison, the values obtained from the modified ABC titration method (ABC titration corrected by boron determined by atomic absorption spectroscopy) are also shown in the figure.

The concentration of the three components in the process liquor did not change significantly during the trial period. The EA concentration obtained by the ATR-UV method agrees well with that obtained by the modified ABC titration method during the entire period, even when borate addition reached 5%. The sulfide and carbonate concentrations measured by the two methods showed a little higher difference, especially toward the end of the three-day period. This difference is mainly due to the fact that the boron correction procedure adopted in the modified ABC titration method uses the same boron value measured once a day in this trial, even though the borate concentration in the process liquor was gradually accumulated throughout the trial. Furthermore, the effect of weak alkali, sodium borate, on the titration values of sulfide and carbonate may be too complicated to correct. It can be seen that the standard deviation of the titration data is much higher than that of the ATR-UV data, especially the sulfide concentration. It should be pointed out that the reproducibility of the sulfide concentration determined by titration during the trial was not very high, about  $\pm 10\%$ .

About 3 month after the trial started, the ATR-UV method was again used to analyze the mill liquor. The borate charge was increased to a final value of about 17% in this second trial. The results obtained from ATR-UV and the modified ABC titration methods are listed

in Table I. The results from the ATR-UV method were calculated using the calibration constants obtained three months previously at the beginning of the first trial using the conventional liquor (without borate). Because the exact time-dependent borate charge was not known, the reported results from ATR measurements were not corrected for the effect of borate. It can be seen from the data even at this higher level of borate loading that the data obtained from ATR-UV sensor for sulfide still qualitatively agree with that obtained by the modified ABC titration method (boron concentration was obtained by sulfide titration using silver nitrate once a day).

## CONCLUSIONS

This work demonstrates that the ATR-UV technique can be used to determine the concentrations of sulfide, EA, and carbonate in kraft white liquors under borate autocausticization operations. It was found that borate does not adsorb UV light. However, if its concentration is high, i.e., 5%, it can cause significant changes in the liquor refractive index, which can affect the absorption values of other compounds. At 5% molar substitution of calcium oxide with borate, the effect of borate on the analysis is negligible. The three-day mill trial indicates that the concentration values determined using ATR-UV method agree well with those measured by the reference method, i.e., the ABC titration method corrected for boron concentration by atomic adsorption analysis. The standard deviation, or scatters, of the values from the ATR-UV method is much lower than that from the modified titration method. Furthermore, the ATR-UV system is very stable. The calibration constants obtained at the beginning of the operation were found still to provide good measurements of sulfide, alkali, and carbonate after 3 months of the operation. Therefore, frequent calibration may not be required in using the ATR-UV method.

## ACKNOWLEDGMENT

This research was supported by the United States Department of Energy (Grant No. DE-FC07-96ID13438).

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Figure 1

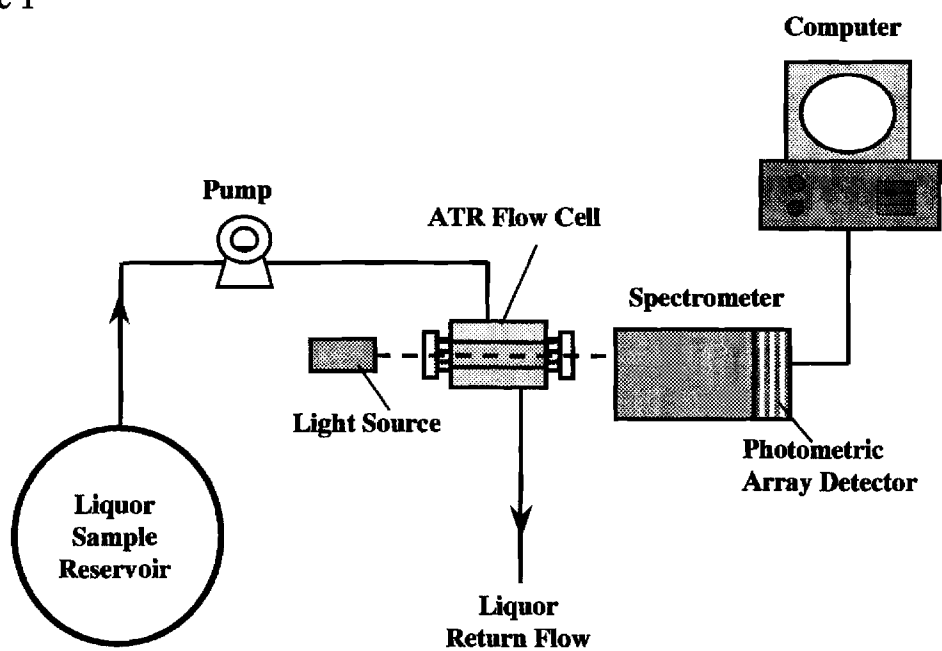


Figure 2

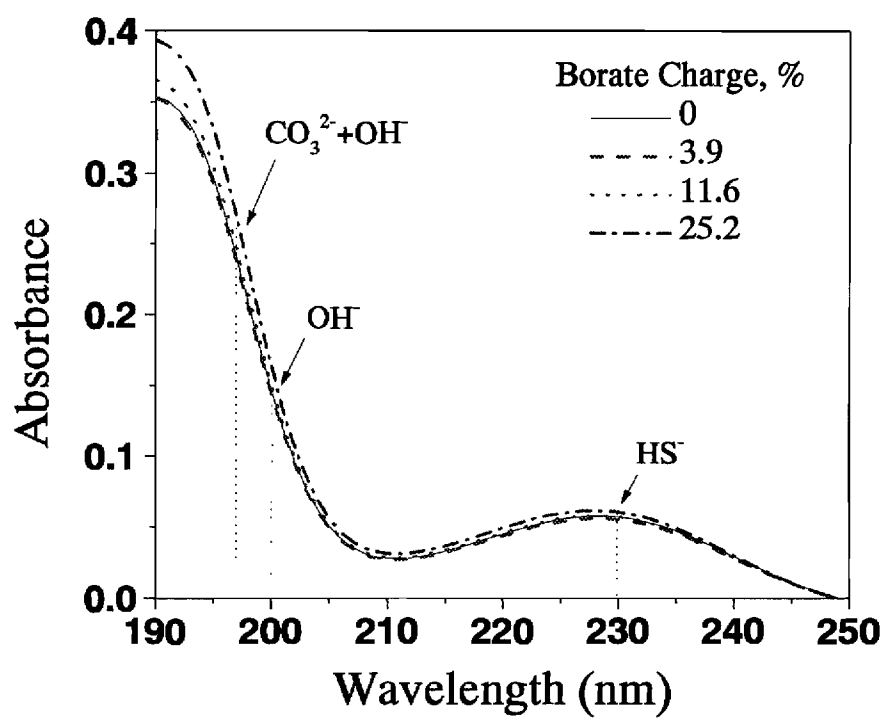




Figure 3

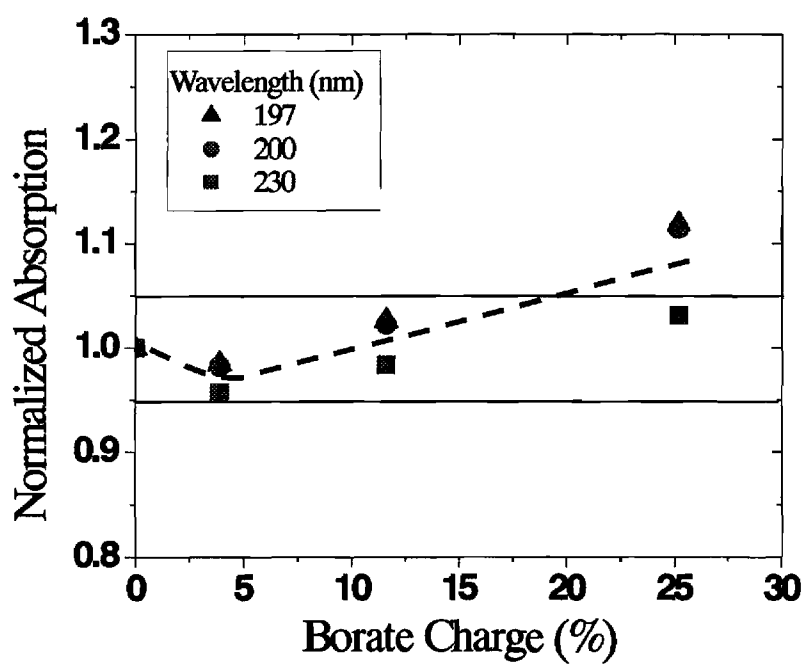


Figure 4

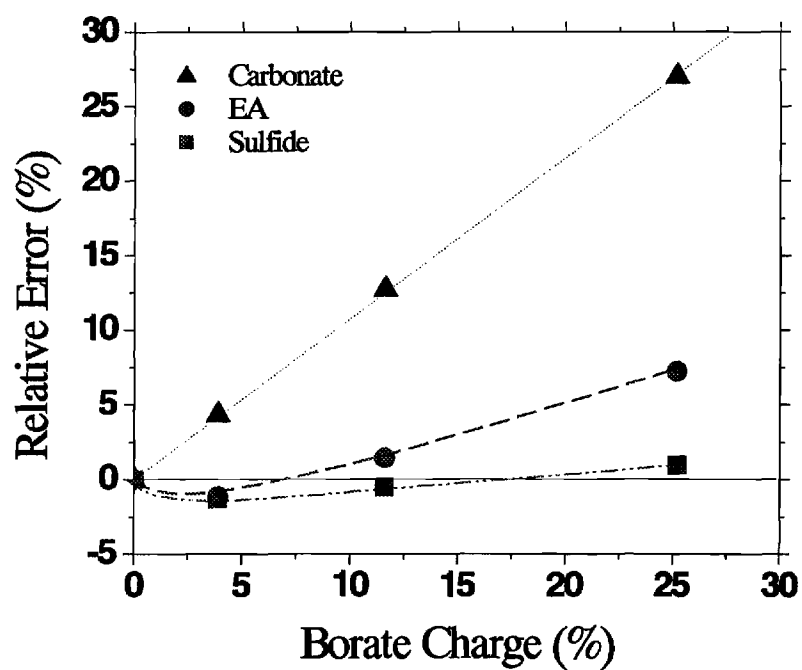


Figure 5

